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STUDY OF ELECTRODE PHENOMENA IN HIGH ENERGY
DENSITY DISCHARGES AS APPLIED TO PLASMA
ACCELERATION PROBLEMS

Contract No. NASW-1103

To: NASA Headquarters
Office of Advanced Research Technology
Research Division
Physics of Fluids Branch, Code RRP
Washington, D. C. 20546

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ABSTRACT

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During this reporting period a large fraction of our efforts was concentrated on the investigation of structural damage in well defined noble metal target structures due to low energy argon ion bombardment. A mechanism of preferred nucleation of argon interstitials at lattice imperfections was discovered which is thought responsible for the disintegration of target structures in preferred areas. It is conceivable that the same mechanism contributes to the known small differences in sputtering yields of materials of varying degrees of crystallographic perfection for ion energies below 500 eV. This effect is not important for high ion energies in conjunction with the destruction of metal surfaces by sputtering attack since the influence of crystallographic orientation is much larger.

First electron microscopy replica studies of copper cathode and anode electrodes of a coaxial plasma gun showed only minor morphological surface damage after short exposures to a nitrogen discharge. Indications are that chemical surface attack - which cannot be investigated properly by replica techniques - is predominant.

It is proposed, therefore, to concentrate future studies on the problem of chemical attack of target surfaces. Both thin film target and bulk electrode studies will be directed toward this end.

Author

I. Low Energy Argon Ion Bombardment of Thin (111)- and (100) Single Crystals and Polycrystals of Gold.

1. Target Specimen Preparation

Gold target films amenable to transmission electron microscopy studies were prepared by epitaxial vacuum deposition techniques. The (111) oriented single crystals were grown on epitaxial silver layers on mica, the (100) oriented crystals on epitaxial silver on NaCl and the coarse polycrystalline gold layers on electrolytically polished bulk silver substrates. The respective substrate temperatures and deposition rates are given in Table 1. These growth conditions were found to result in target films that became coherent during very early stages of overgrowth and, therefore, turned out to be very uniform in thickness. The uniformity in thickness was necessary to permit unambiguous interpretation of disintegration results. Figure 1a and 1b represent respective examples of polycrystalline gold films: 1a was grown on quartz at elevated substrate temperatures and shows many small grains still separated by occasional holes in the film while 1b was grown according to Table 1 and shows larger grains and is uniform in thickness.

The high degree of single crystallinity of the target films is demonstrated by Fig. 2, an electron diffraction pattern of a (111) oriented gold target.

Orientation of Au Targets	Substrate for Epitaxial Growth	Intermediate Layer of Ag		Final Layer of Au	
		Substr. Temp	Depos. Rate	Substr. Temp.	Depos. Rate
(111)	mica	280°C	600 Å/min	350°C	1200 Å/min
(100)	NaCl	250°C	700 Å/min	250°C	700 Å/min
Polycryst	Bulk Ag (el. pol.)	250°C	700 Å/min	250°C	700 Å/min

TABLE 1

2. Radiation Damage and Etching

Gold target films of 600 \AA to 700 \AA thickness were subjected to bombardment with Ar^+ ions of energies ranging from 100 eV to 500 eV. Since, however, the observed radiation damage effects were essentially independent of ion energy and it was not the purpose of this work to measure sputtering yields quantitatively all of the work reported was carried out at 500 eV. The irradiation times ranged from 5 min to 20 min, mostly around 10 min, but the time of bombardment is not an important parameter in these studies because of the appreciable differences of ion beam densities within the target area.

The Fig.'s 3a, 3b, and 3c show radiation damage effects in (111), (100) and polycrystalline Au targets as revealed by transmission electron microscopy techniques. For reasons of comparison Fig. 3d is added in which most of the damage seen in the form of dark dots and short dark dislocation lines was removed by subsequent heat treatment.

The nature of this type of radiation damage was studied in detail by others* and defined as interstitial point defect clusters and subsurface dislocations. The damage is localized at the surface of the target to a depth of about 100 \AA (for 500 eV Ar^+ ions) and formed by direct impingement of replacement sequences aided by local thermal activation from displacement spikes in the gold lattice. It is plausible to assume that a slow single interstitial is created during bombardment with an energy of migration not less than 0.7 eV.

In target areas where the impinging Ar^+ ion flux was higher, however, the structure of the Au targets is quite different (Fig.'s 4a, 4b). As a

*J. A. Venables, R. W. Baluffi, *Phil. Mag.* 11, (1965), 1021.

P. Bowden, D. G. Brandon, *Phil. Mag.* 9, (1963), 935.

result of the high irradiation dose in these areas holes are etched into the target the three-fold (for (111) orientation) or four-fold (for (100) orientation) symmetry of which is directly related to the crystallographic structure of the target film. It will also be noted that the predominant lattice defects visible in these micrographs, namely microtwins, stacking faults and coherent twin boundaries, extend along directions which are parallel to the edges of the holes. This behavior shall be explained later in terms of preferred nucleation of argon interstitials at these lattice defects.

3. Heat Treatment of Target Foils after Bombardment

The use of an electron microscope specimen heating stage in connection with the ion gun permits heat treatment of the target specimens immediately after bombardment and observation of respective changes in the specimen microstructure. With the help of this technique tiny round and bright spots were found to appear in the target structure. They grow in size during annealing times of 30 min and longer. Similar features had been observed before* and are identified as micro argon gas bubbles formed by the clustering of injected argon interstitials which become mobile at elevated target temperatures (350°C annealing temperature).

The important new feature observed on these argon clusters is their preferred precipitation at coherent twin boundaries, microtwins, grain boundaries, and dislocations. This is demonstrated by Fig. 5a (111)-orientation), Fig. 5b (polycryst. Au film) and Fig. 5c which is a higher magnification of 5a. A similar behavior is observed in (100) films.

*R. S. Nelson, Phil Mag. 10, (1964), 343.

This result can be explained in terms of heterogeneous nucleation theory concepts. Here a further free energy term is introduced - in addition to the thermodynamic driving force for homogeneous nucleation - which stems from strain energy release at lattice distortions.* Consequently, lattice defects and grain boundaries will be locations of preferred nucleation and since the diffusion of argon interstitials is thought to be controlled by the diffusion of lattice vacancies the preferred nucleation of argon interstitials is also an indication of the nucleation behavior of vacancies. Our results are, therefore, in good agreement with related work on the precipitation of vacancies at grain boundaries.

4. Sputtering Yield Considerations

In applying this mechanism of preferred nucleation of injected gas interstitials at lattice defect sites to the problem of disintegration of metal targets by sputtering attack one cannot escape the conclusion that these lattice defect sites should also be locations for preferred sputtering attack. This is demonstrated in a striking way by the formation of holes of well defined shape by ion bombardment (see Fig.'s 4a and 4b) and by preferred grain boundary attack in polycrystal gold, Fig. 4c. Whether, however, this effect is large enough to influence the macroscopic sputtering yield of bulk metal targets - eventually by secondary effects of increased angle of ion incidence at preferably etched locations - cannot be assessed with the present experimental technique. It is conceivable that the appreciable differences in the sputtering yield of polycrystals at low ion energies might be explained in this way (see Fig. 6). For high ion energies the differences in sputtering yield as a function of

*J. W. Cahn, ACTA METALL., 5, (1957), 169.

crystallographic orientation are so predominant* (see Fig. 7) that a significant influence of the microstructure is very unlikely.

In order to demonstrate these considerations graphically a recently published compilation of sputtering yield data is given in Fig. 6 and Fig. 7.** Although the data of Fig. 6 and Fig. 7 apply to copper the general trend of the sputtering yields should also hold for gold, another f.c.c. crystal. The graphs show very clearly the wide spread in sputtering yields for polycrystalline targets at low and high energies and the appreciable differences in single crystal yields as a function of orientation for ion energies higher than 500 eV.

We have verified the fact that in the energy range from 100 eV to 500 eV the sputtering yield differences for gold as a function of crystallographic orientation are very small:

- (a) Separate single crystal gold films of (111) - and (100) - orientation were bombarded with 500 eV argon ions for the same length of time and their thicknesses before and after bombardment were measured by transmission electron microscopy techniques; (the width of microtwins - visible as dark bands in the micrographs - are a direct measure for the film thickness if the crystallographic orientation of the film plane is known). Since the ion current densities in small target areas cannot be measured with sufficient accuracy it was impossible to determine absolute sputtering yields in this way, but relative values were determined:

$$\frac{\text{Sputtering yield (100) - gold}}{\text{Sputtering yield (111) - gold}} = 87\%$$

*G. D. Magnuson, C. E. Carlston, J. Appl. Phys. 34, (1963), 3267.

A. L. Southern, W. R. Willis, M. T. Robinson, J. Appl. Phys. 34, (1963), 153.

**E. J. Zdanuk, S. P. Wolsky, J. Appl. Phys. 36, (1965), 1683.

- (b) The uncertainty concerning ion current density variations over small target areas can be eliminated if thickness variations due to sputtering are measured in adjacent microscopically small gold grains of (100) - and (111) - orientation. Such grains were found in our polycrystalline gold films and the result for 500 eV ion energy was again:

$$\frac{\text{Sputtering yield (100) - gold}}{\text{Sputtering yield (111) - gold}} = 90\%$$

- (c) Because of the small differences in sputtering yields at low ion energies for (100) - and (111) - gold grains it was not surprising to find that in none of our polycrystalline targets bombarded almost to destruction with energies from 100 eV to 500 eV there was any sign of appreciable preferred etching of whole grains of a certain crystallographic orientation. This included orientations other than (100) and (111).

One, therefore, has to conclude from these experiments that for ion energies lower than 500 eV and f.c.c. metals the influence of crystallographic orientation on disintegration of polycrystal metal targets is negligible for practical purposes. Indications are that also in the low ion energy region distorted lattice sites (grain boundaries in particular) favor localized disintegration of metal target surfaces.

II. Investigation of Bulk Electrode Surfaces

The surface structure of the copper anode and cathode of a coaxial plasma gun (1.5" I.D., 5" O.D., 5.5 cm length) of Dr. A. V. Larson's Plasma Propulsion Group at General Dynamics/Convair was studied by replica electron microscopy. The gun (pulse line total capacitance: 184 μf ,

charging voltage: 1kV, pulse time: few μ sec, propellant: nitrogen, propellant density at moment of discharge: 10^{16} particle/cm³) was fired 67 times before visible deterioration of the electrode surfaces initiated. At this point the electrode surfaces were replicated.

Figure 8 is a large area low magnification light microscope picture of the cathode surface showing definite localized discharge patterns streaked in the direction of gas flow. From pictures of this type and from the amount of visible surface deterioration, it was expected to find rather rough surface structures with higher resolution micrographs. However, this was not the case, as documented by the electron micrographs of Figs. 9a and 9b. The surprisingly small degree of surface roughness was practically identical in nature for both anode and cathode electrode surfaces. Although there is much room for speculation as to the nature of the surface processes which could cause morphological changes of this sort indications are that chemical surface attack rather than sputtering effects are to be held responsible for the observed surface damage. Future work will have to be concentrated in this area.

III. Proposed Future Studies

The question of possible chemical attack of copper electrode surfaces in high energy density nitrogen discharges needs clarification and currently used replica-electron microscopy methods are inadequate for this purpose.

It is, therefore, proposed to conduct the following studies:

- (a) Investigation of the surface structure and chemical composition of small samples of bulk discharge electrodes by reflexion electron diffraction and electron microprobe methods.
- (b) Nitrogen ion bombardment of thin film copper targets inside the electrode microscope and evaluation of results by transmission electron microscopy and diffraction techniques.

Illustrations

Figure No.

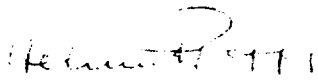
- 1a. Polycrystalline gold target film grown on quartz, 65000 X.
- 1b. Polycrystalline gold target film grown on bulk silver, 65000 X.
2. Transmission electron diffraction pattern of single crystal (111)-gold film.
3. Ion radiation damage in (a) (111) - Au, 130000 X, (b) (100) - Au, 130000 X, (c) polycrystalline Au, 65000 X.
- 3d. Radiation damage removed from (111) - Au target by 350°C anneal after ion bombardment, 130000 X.
4. Holes etched into target films by extensive argon ion bombardment, (a) (111) - Au, 130000 X; (b) (100) - Au, 130000 X.
- 4c. Preferred grain boundary attack in polycrystalline gold, 65000 X.
5. Preferred nucleation of argon interstitials at lattice defects in (a) (111) - Au, 65000 X, (b) polycrystalline Au, 130000 X, (c) (111) - Au, 360000 X.
6. Low energy argon ion sputtering yields for single crystal and polycrystal copper (after Zdanuk and Wolsky).
7. High energy argon ion sputtering yields for single crystal and polycrystal copper (after Zdanuk and Wolsky).
8. Light micrograph of bulk copper cathode surface after 67 discharges, 150 X.
9. Replica electron micrographs of bulk copper electrodes after 67 discharges, (a) 15000 X, (b) 33000 X.

List of Man Hours Worked During the Reporting Period

During the second three months of work on NASA contract No. NASW-1103
the following man hours were charged:

Technician	400 hours
Staff Scientist	400 hours

San Diego, Calif.
August 8, 1965



Helmut Poppa
Principal Investigator

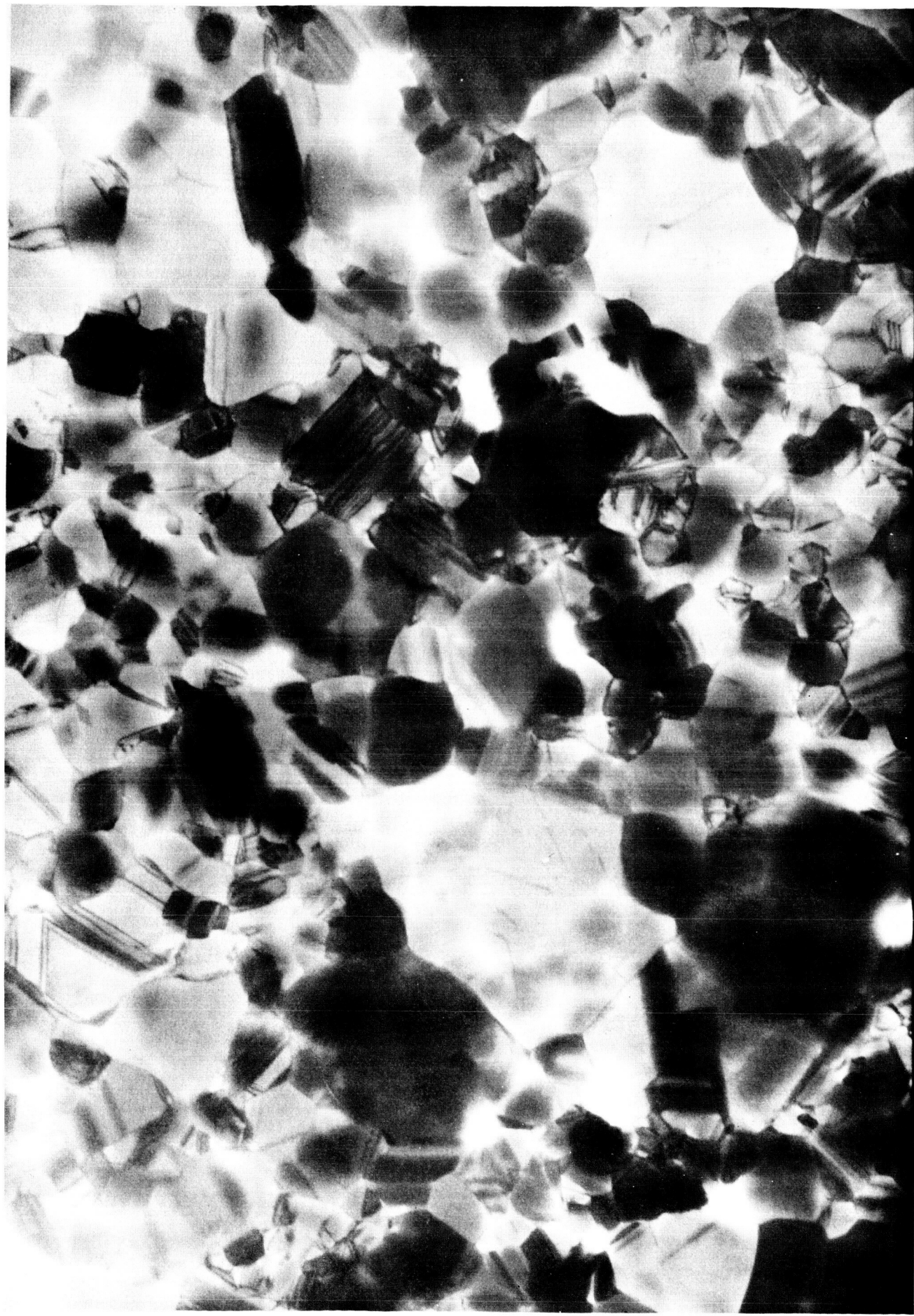


Fig. 1a

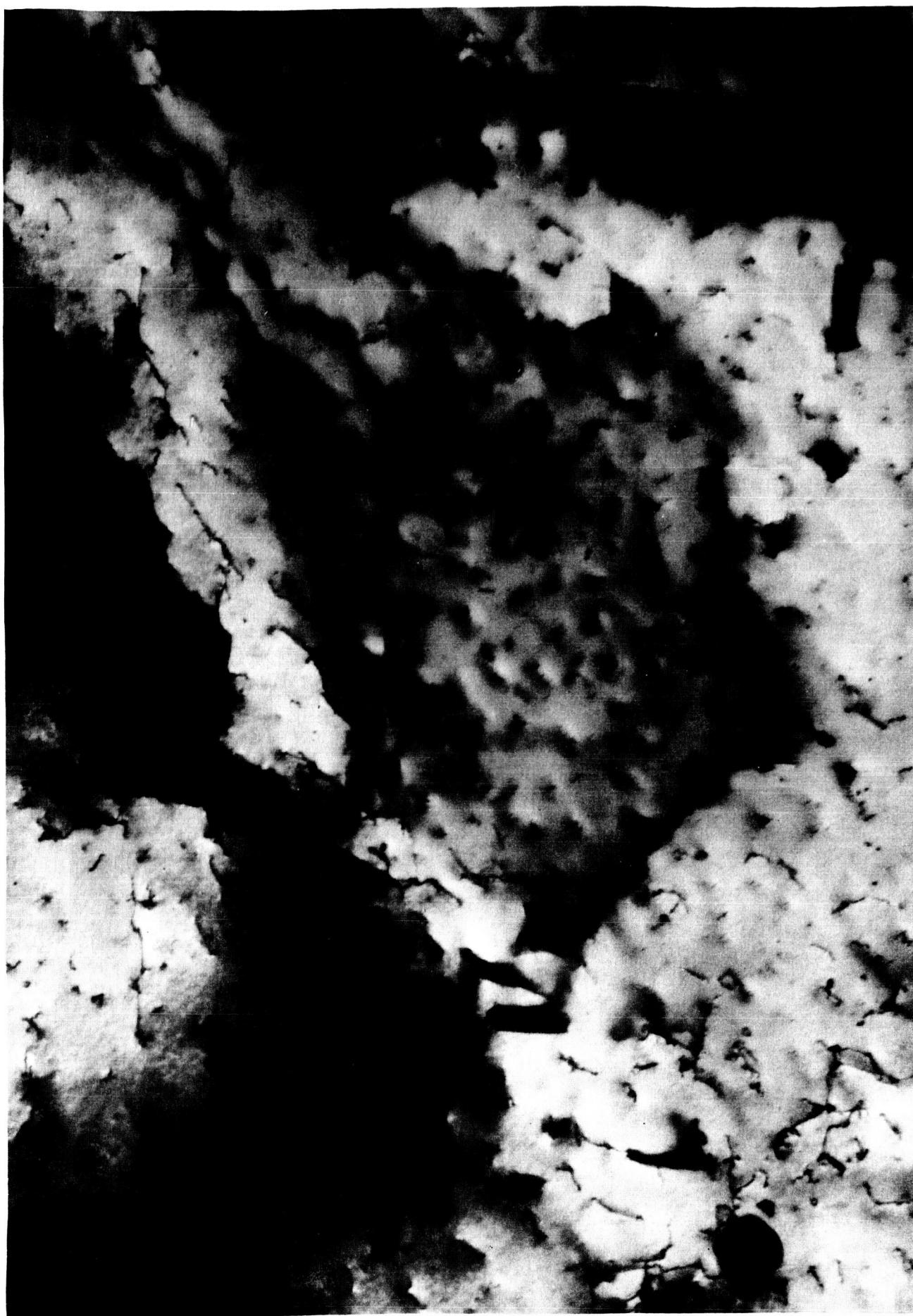


Fig. 1b

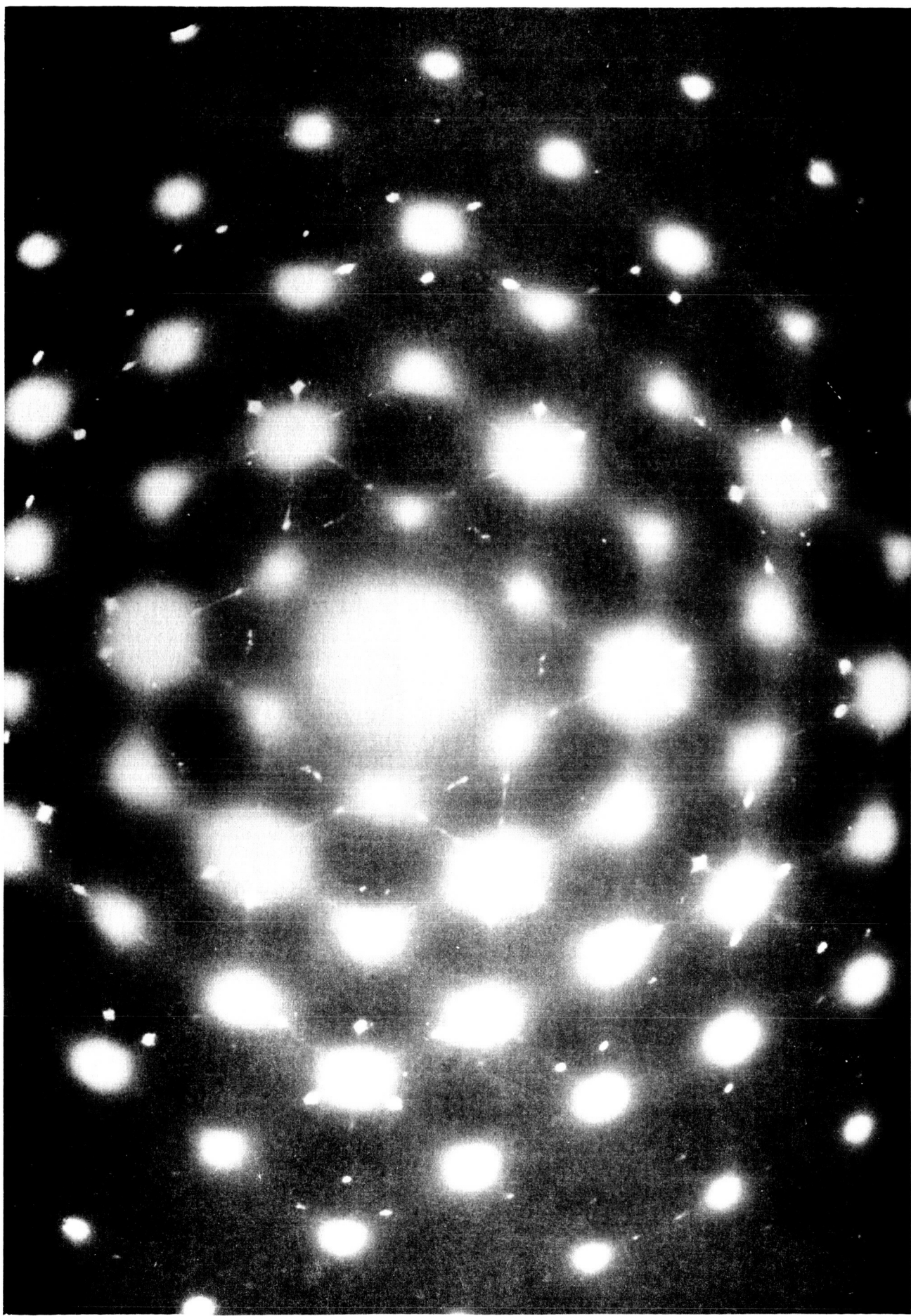


Fig. 2

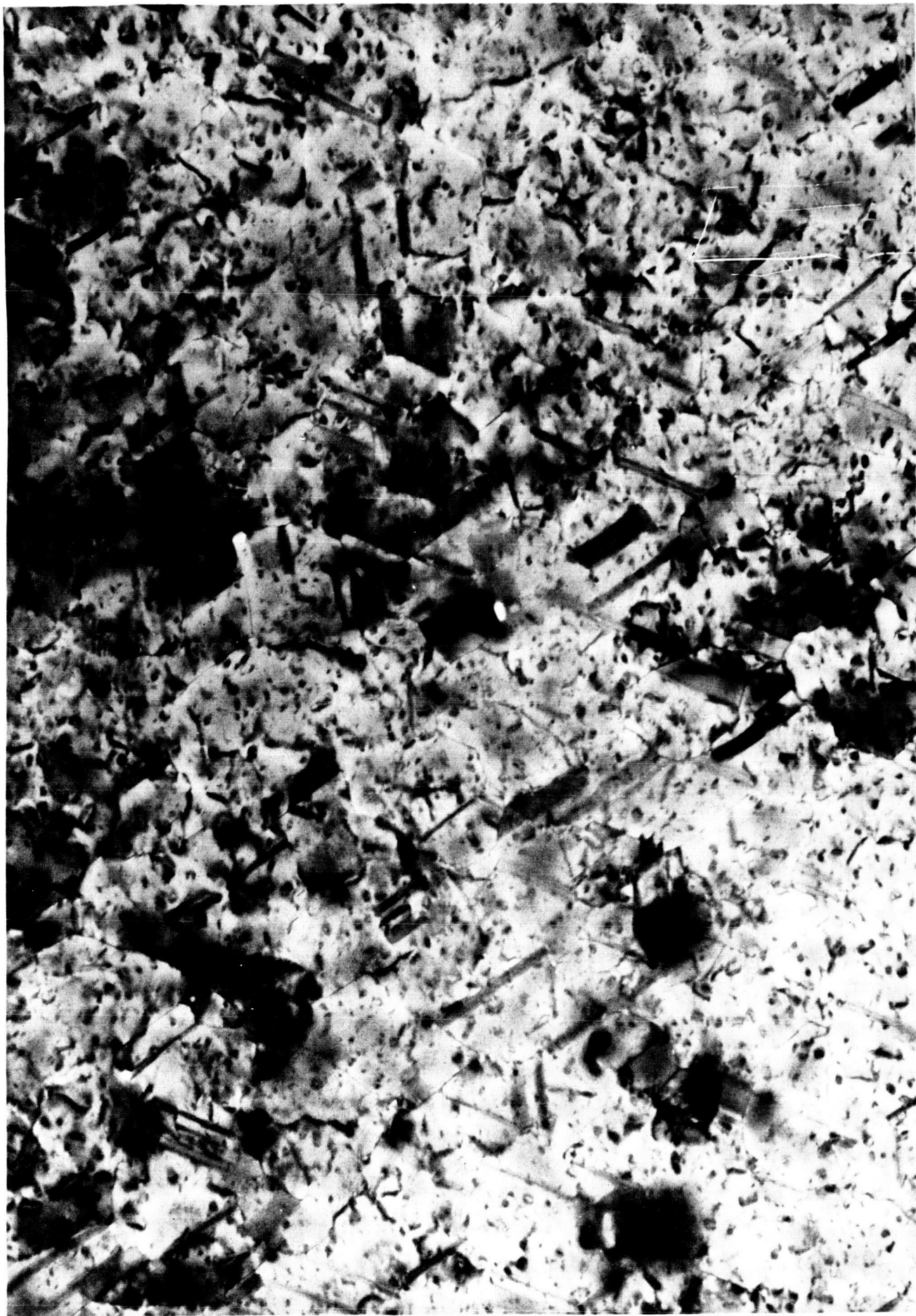


Fig.3a

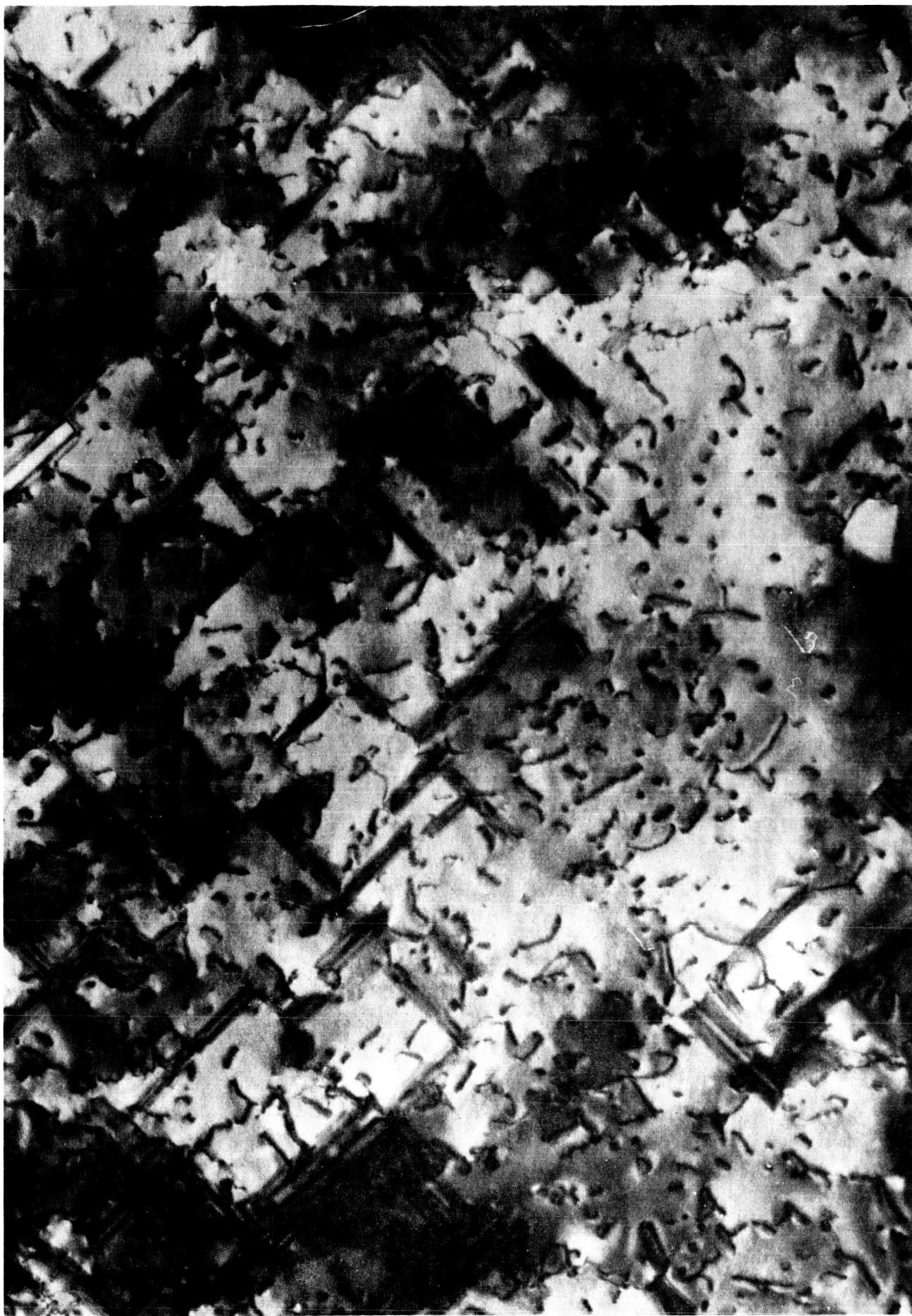


Fig.3b



Fig.3c



Fig.3d

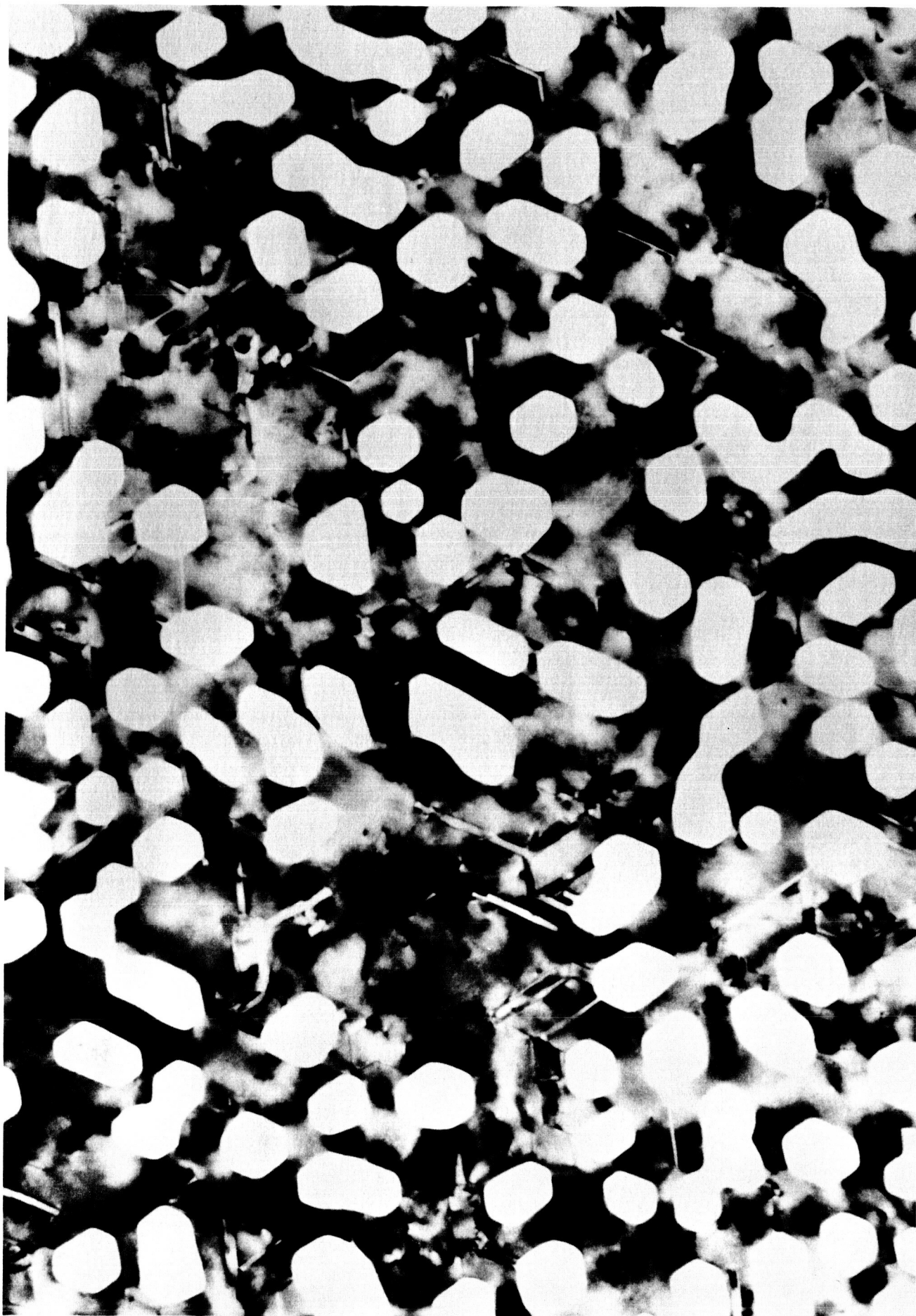


Fig. 4a

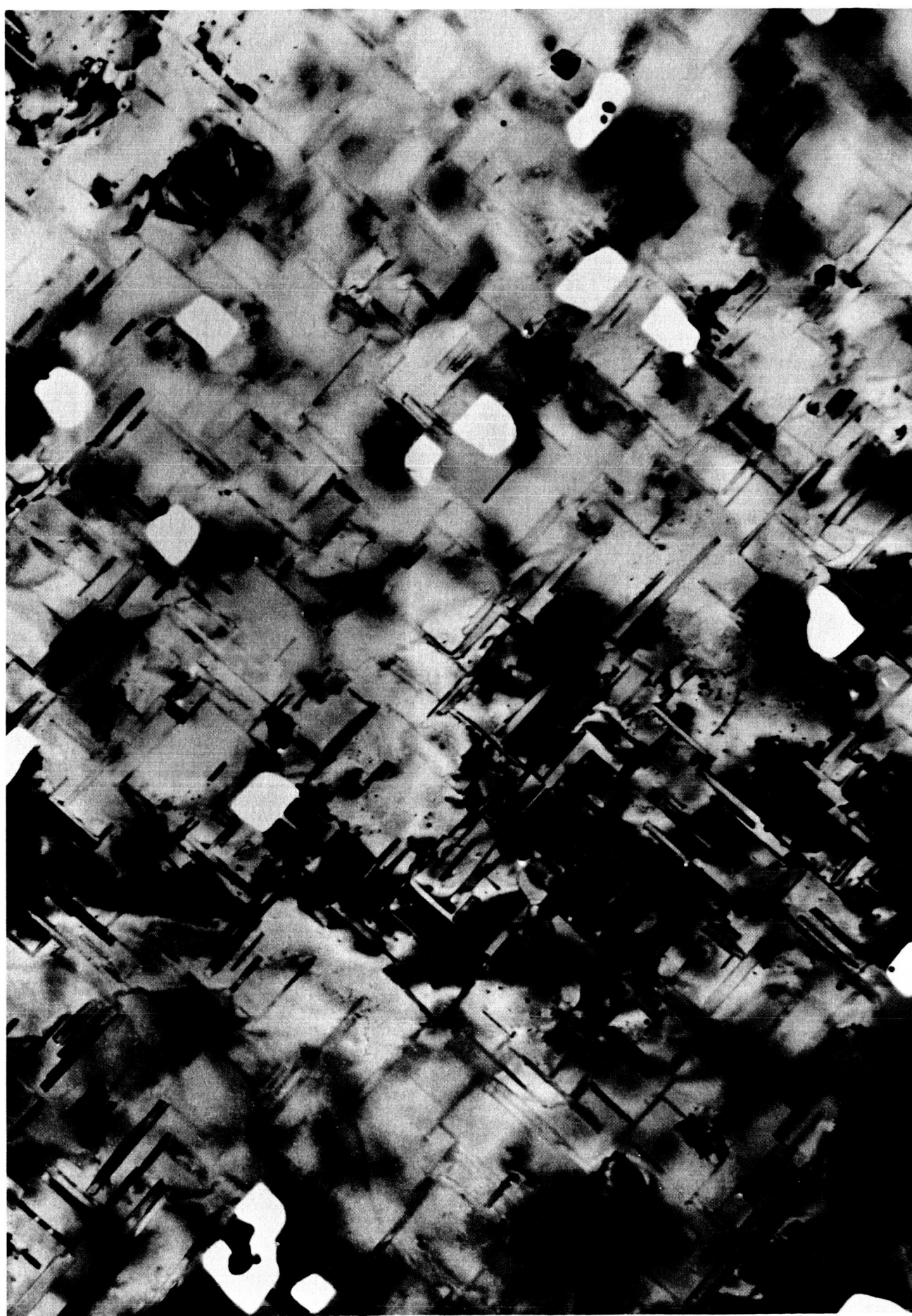


Fig. 4b



Fig. 4c



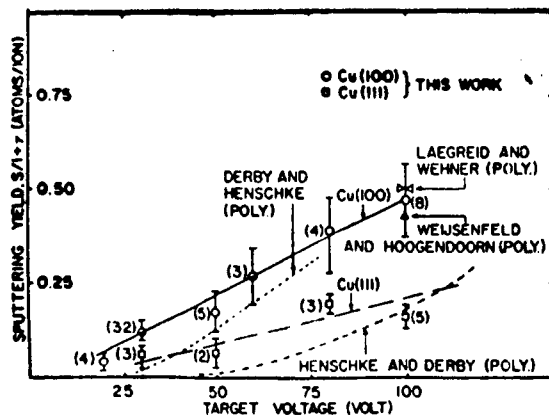
Fig. 5a



Fig. 5b



Fig. 5c



Sputtering yield of (100) and (111) copper from 20-100 eV.

Fig.6

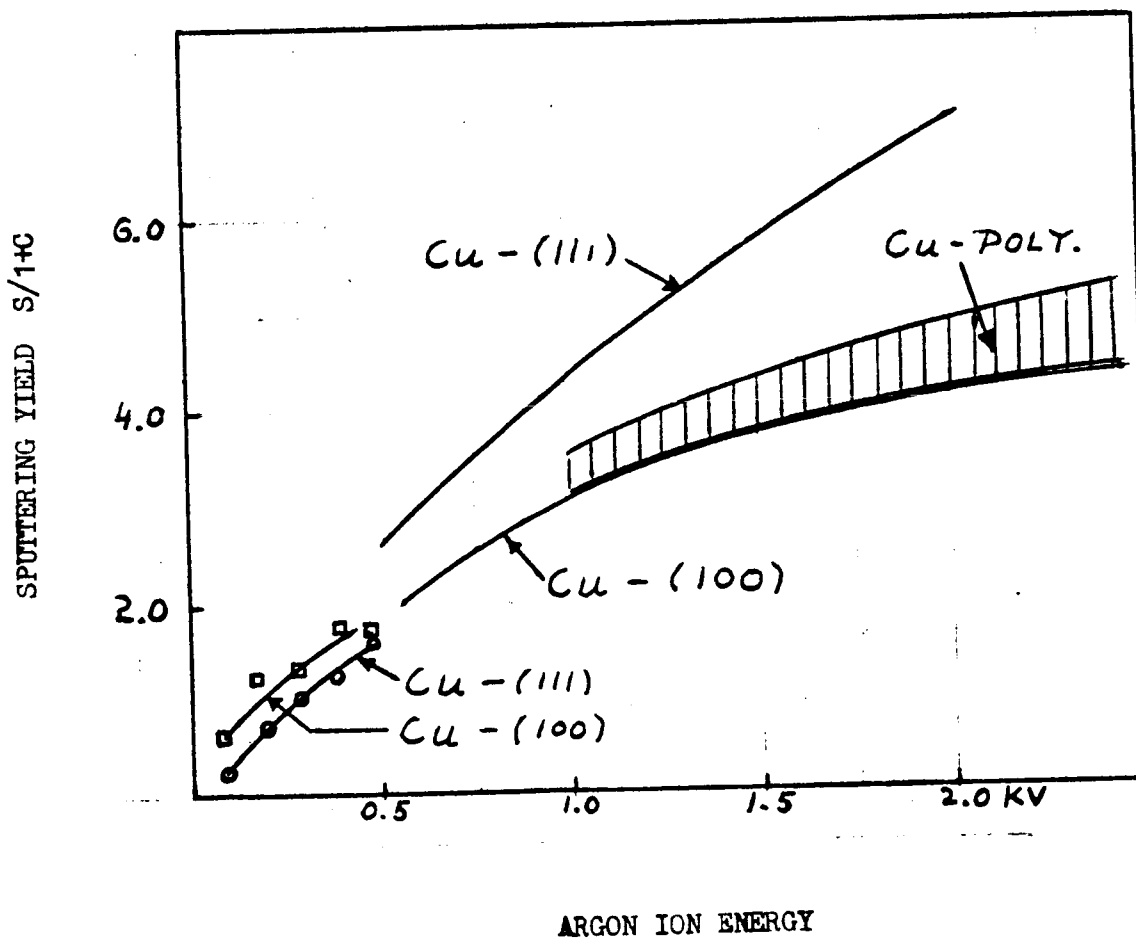


Fig.7



Fig.8



Fig. 9a



Fig. 9b